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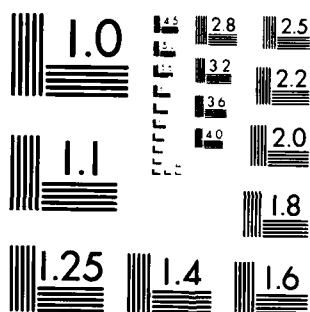
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AN EXACTLY SOLVABLE MODEL FOR IDEALLY POLIRIZABLE INTERFACES

by

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ABSTRACT

A model for the interface of two interacting one component plasmas of different background densities separated by an impermeable surface, is solved exactly in two dimensions at one special temperature. This model emulates the behaviour of an ideally polarizable interface. We obtain density profiles, differential capacity and surface tension as a function of the applied potential. Pertinent sum rules are given.

I INTRODUCTION

A model for a charged interface has been proposed recently [1,2] in which two media described by classical, one component plasmas (OCP) of different background densities are separated by a charged gap. Although this model is far from a realistic description of the metal-electrolyte interface, it has the interesting feature that an exact solution can be found in two dimensions for the special reduced temperature of 2, using the method of Jancovici and coworkers [3]. On the other hand, as shown in [1], it appears that this model does not allow any change of the potential drop across the interface with the surface charge, and in this sense emulates the behaviour of a non-polarizable interface. This is a result of the fact that charged particles can move freely across the interface, which, because of perfect screening, is probably connected to the non-existence of long range correlations along the interface [1,2].

In the present note we consider another physically interesting situation corresponding to the polarizable interface, such as the classical example of the mercury-aqueous electrolyte solution interface. For that purpose, we assume that between the two media there is an impermeable surface which prevents the ions from crossing the interface while allowing electrical interactions between all particles. Clearly, this model is consistent with the concept of the ideally polarizable electrode [4]. A full description of the technical details of our solution will be given in a forthcoming paper. Here we give only a summary of our main results.

II- PARTITION FUNCTION: METHOD OF SOLUTION

Our system consists of two concentric circles of radii R_1 and R_2 . The inner region ($0 < r < R_1$) has background charge density $-e\alpha_1/\pi$, where e is the elementary charge, and contains N_1 particles of charge e . We want to allow for an excess charge density $-e\sigma/\pi$ along the wall then we must have

$$N_1 = \alpha_1 R_1^2 - 2\sigma R_1 \quad (1)$$

The outer region ($R_1 < r < R_2$) has background density $-e\alpha_2/\pi$, excess charge density $e\sigma/\pi$ and contains N_2 particles of charge e . Hence

$$N_2 = \alpha_2 (R_2^2 - R_1^2) + 2\sigma R_1 \quad (2)$$

The plasma coupling parameter is

$$\Gamma = \beta e^2 = 2$$

where $\beta = 1/kT$ is the thermal Boltzmann factor and T is the temperature

The potential energy of the system is

$$V = V_0 + \frac{1}{2} e^2 \left\{ - \sum_{i>j}^N \ln |\vec{r}_i - \vec{r}_j|^2 + \alpha_1 \sum_{i=1}^{N_1} (r_i^2 - R_1^2) + \alpha_2 \sum_{i=N_1+1}^N (r_i^2 - R_1^2) + (\alpha_1 - \alpha_2) R_1^2 \sum_{i=N_1+1}^N \ln \left(\frac{r_i}{R_1} \right)^2 \right\} \quad (3)$$

where V_0 is a constant background term and $N = N_1 + N_2$. Note that the charge density $e\sigma$ does not appear explicitly.

Following the method introduced by Jancovici [3], the canonical partition function can be written

$$\begin{aligned} Z_{N_1, N_2} &= \frac{1}{N!} \int d\mathbf{r}^N e^{-\beta V} \\ &= e^{-\beta V_0} \frac{(2\pi)^N}{N!} \int_0^{R_1} d\mathbf{r}^{N_1} e^{-\alpha_1 \sum_{i=1}^{N_1} (r_i^2 - R_1^2)} \int_{R_1}^{R_2} d\mathbf{r}^{N_2} e^{-\alpha_2 \sum_{i=N_1+1}^N (r_i^2 - R_1^2)} \prod_{i=N_1+1}^N \left(\frac{r_i}{R_1} \right)^{2(\alpha_2 - \alpha_1) R_1^2} \\ &\quad \cdot \sum_{\mathcal{P}} \mathcal{P} [r_1^0 r_2^2 r_3^4 \dots r_N^{2(N-1)}] \end{aligned} \quad (4)$$

where \mathcal{P} is the permutation operator between the N particles.

Since the ions are not allowed to cross the inner circle, it will be useful to introduce a factor z which, as we will see later, fixes the ratio of the activities on both sides of the interface.

Z_{N_1, N_2} can then be written as a contour integral

$$Z_{N_1, N_2} = e^{-\beta V_0} (2\pi)^N \frac{1}{2i\pi} \oint \prod_{n=0}^{N-1} [z \phi^1(n) + \phi^2(n)] \frac{dz}{z^{N_1+1}} \quad (5)$$

where

$$\phi^1(n) = \frac{e^{\alpha_1 R_1^2}}{\alpha_1^{n+1}} \gamma(n+1, \alpha_1 R_1^2)$$

$$\phi^2(n) = \frac{e^{\alpha_2 R_1^2}}{\alpha_2^{n_2+1} R_1^{2(n_2-n)}} [\gamma(n_2+1, \alpha_2 R_2^2) - \gamma(n_2+1, \alpha_2 R_1^2)]$$

with $n_2 = n + (\alpha_2 - \alpha_1) R_1^2$

and $\gamma(n+1, R^2) = \int_0^{R^2} e^{-u} u^n du$

is the incomplete gamma function. It is convenient to write (5) in the form

$$Z_{N_1, N_2} = Z_{N_1} Z_{N_2} \Xi \quad (6)$$

with

$$\Xi = \frac{1}{2i\pi} \oint \frac{dz}{z} \prod_{n=1}^{N_1} [X(n) z^{-1} + 1] \prod_{n=N_1+1}^N [X(n)^{-1} z + 1]$$

where

$$X(n+1) = \frac{\phi^2(n)}{\phi^1(n)}$$

Z_{N_1} and Z_{N_2} are the partition functions for the uncoupled inner and outer regions, and are introduced to insure proper convergence of the integrals below.

Define

$$\gamma(z) = \sum_{n=1}^{N_1} \ln [\chi(n) z^{-1} + 1] + \sum_{n=N_1+1}^N \ln [\chi(n)^{-1} z + 1] \quad (7)$$

In the limit $R_2, R_1 \rightarrow \infty$, the interface becomes a straight line, and we get

$$\gamma(z) \sim R_1 \sqrt{2\alpha_1} \left[\int_{-\infty}^{\sigma \sqrt{1/2\alpha_1}} \ln \left[\frac{z + \chi(t)}{\chi(t)} \right] dt + \int_{\sigma \sqrt{1/2\alpha_1}}^{\infty} \ln \left[\frac{z + \chi(t)}{z} \right] dt \right] \quad (8)$$

where

$$\chi(t) = m e^{\frac{(m^2-1)t^2}{2}} \frac{\operatorname{erfc}(mt)}{\operatorname{erfc}(-t)}$$

and $m = \sqrt{\alpha_1/\alpha_2}$

In this limit Ξ can be evaluated asymptotically by the method of steepest descents, choosing a contour $z = z_0 \exp(i\theta)$. We find

$$\Xi \sim \frac{e^{\gamma(z_0)}}{z_0 \sqrt{2\pi} \gamma'(z_0)} \quad (9)$$

where z_0 is the position of the saddle point in the complex z -plane.

z_0 is real and is computed from

$$\int_{\sigma \sqrt{1/2\alpha_1}}^{\infty} \frac{\chi(t)}{\chi(t) + z_0} dt = \int_{-\sigma \sqrt{1/2\alpha_1}}^{\infty} \frac{z_0}{\chi(-t) + z_0} dt \quad (10)$$

For $m=1$ we have

$$z_0(-\infty) = z_0(\infty)^{-1}$$

so that $z_0(\infty) = 1$

In the general case, (10) must be solved numerically.

III-DENSITY PROFILE

The density $\rho(r)$ can be obtained by the same method. After some manipulations we get

$$\rho(r) = \frac{1}{\pi} \frac{1}{[-]} \sum_{n=1}^N f_n^1(r) \frac{1}{2i\pi} \oint dz \frac{e^{Y(z)}}{z + X(n)} \quad \text{for } r < R_1 \quad (11)$$

where

$$f_{n+1}^1(r) = \frac{e^{-\alpha_1(r^2 - R_1^2)} r^{2n}}{\phi^1(n)}$$

and

$$\rho(r) = \frac{1}{\pi} \frac{1}{[-]} \sum_{n=1}^N f_n^2(r) \frac{1}{2i\pi} \oint \frac{dz}{z} e^{Y(z)} \frac{X(n)}{z + X(n)} \quad \text{for } r > R_2 \quad (12)$$

where $f_{n+1}^2(r) = \frac{e^{-\alpha_2(r^2 - R_1^2)} r^{2n_2}}{\phi^2(n) R_1^{2(n_2 - n)}}$

In the limit $R_2, R_1 \rightarrow \infty$ and taking the origin of coordinates at the wall ($x = r - R_1$), we get

$$\rho(x) = \begin{cases} \frac{2\alpha_1}{\pi^{3/2}} z_0 \int_{-\infty}^{+\infty} \frac{e^{-(t+x\sqrt{2\alpha_1})^2}}{z_0 \operatorname{erfc}(-t) + m e^{(m^2-1)t^2} \operatorname{erfc}(mt)} dt & x < 0 \\ \frac{2\alpha_1}{\pi^{3/2}} \int_{-\infty}^{+\infty} \frac{e^{-(mt+x\sqrt{2\alpha_2})^2}}{m \operatorname{erfc}(mt) + z_0 e^{(1-m^2)t^2} \operatorname{erfc}(-t)} dt & x > 0 \end{cases} \quad (13)$$

The integrals in (13) can be computed numerically. The results for one typical case are shown in Figure 1. For $m=1$ the contact densities have the simple expressions

$$\rho_2(0) = \frac{1}{z_0} \rho_1(0) = \frac{\alpha_1}{\pi} \frac{1}{z_0 - 1} \ln z_0 \quad (14)$$

Unlike the case of the permeable [1,2] interface, the density has now a jump at the interface. Notice also that for zero charge and $m=1$, the density remains constant everywhere.

IV-POTENTIAL DROP AND DIFFERENTIAL CAPACITY

The total potential drop across the interface $\Delta\phi = \phi(\infty) - \phi(-\infty)$ can be calculated by integration of the density profile. However, this is not necessary, since $\Delta\phi$ is directly connected to z_0 which is the ratio of the activities. Indeed we have

$$z_0 = e^{\beta[\mu_1 - \mu_2 + e\Delta\phi]} = m e^{-2\Delta\phi/e} \quad (15)$$

where μ_1 and μ_2 are the chemical potentials on each side. In fact it appears that $\Delta\phi$ is the true external variable controlling the state of the system. This is a very nice feature of this model, because this is actually what happens in the electrochemical measurements where the potential is externally fixed. For a given $\Delta\phi$, z_0 is obtained from (15), and the charge density from (10). Alternatively, using the electroneutrality condition, we have a simpler way of calculating $e\sigma$

$$\begin{aligned} \frac{e\sigma}{\pi} &= \int_0^\infty [\rho(x) - \frac{\alpha_1}{\pi}] dx = - \int_{-\infty}^0 [\rho(x) - \frac{\alpha_1}{\pi}] dx \\ &= \frac{\sqrt{\alpha_1}}{2\pi\sqrt{2}} \int_{-\infty}^{+\infty} \operatorname{erfc}(-t) \frac{m e^{m^2 t^2} \operatorname{erfc}(mt) - z_0 \operatorname{erfc}(t) e^{t^2}}{m e^{m^2 t^2} \operatorname{erfc}(mt) + z_0 \operatorname{erfc}(-t) e^{t^2}} dt \end{aligned} \quad (16)$$

Eq. (16) can be shown to be completely equivalent to (10).

The differential capacity $C = \frac{\partial(e\sigma/\pi)}{\partial(\Delta\phi)}$ is now obtained in closed form from (16)

$$C(\Delta\phi) = \frac{z_0}{\pi} \sqrt{2\alpha_1} \int_{-\infty}^{+\infty} \frac{\chi(t)}{[z_0 + \chi(t)]^2} dt \quad (17)$$

A typical curve showing the dependence of C with potential is shown in Figure 2.

For $m=1$, $C(\Delta\phi=0) = \frac{1}{\pi} \sqrt{\alpha_1/\pi}$

V-THERMODYNAMICS AND SUM RULES

From (6) and (8) the surface excess Helmholtz free energy can be calculated. We get

$$\begin{aligned} f^s &= f_o^s - \lim_{R_1 \rightarrow \infty} \frac{1}{\beta 2\pi R_1} \ln \square \\ &= f_o^s - \frac{e^2 \sqrt{2\epsilon_1}}{4\pi} \left[\int_{-\infty}^{\sigma \sqrt{2\epsilon_1}} dt \ln \left[\frac{z_o + \chi(t)}{\chi(t)} \right] + \int_{\sigma \sqrt{2\epsilon_1}}^{\infty} dt \ln \left[\frac{z_o + \chi(t)}{z_o} \right] \right] \end{aligned} \quad (18)$$

where f_o^s is the surface excess free energy of the uncoupled system. Differentiating with respect to the surface charge density, we find the first sum rule

$$\frac{\partial f^s}{\partial (\sigma/\pi)} = \mu_z - \mu_1 + e \Delta \phi \quad (19)$$

It may be shown that this equation is equivalent to the statement that our model satisfies Lippmann's equation

$$\left(\frac{\partial \gamma}{\partial \Delta \phi} \right)_{\mu, T} = -e \frac{\sigma}{\pi} \quad (20)$$

where γ is the surface tension defined by

$$\gamma = \left(\frac{\partial F}{\partial A} \right)_{\mu, T, V, Q} \quad (21)$$

where $Q = e\sigma A$ is the surface charge.

A similar result holds for the case of a OCP near a charged plane [5,6]. Figure 3 shows the dependence of the surface tension with potential (electrocapillarity curve).

Another sum rule can be derived by thermodynamic arguments:

$$P_1 - P_2 = kT [f_1(\phi) - f_2(\phi)] + e \frac{\epsilon_1}{\pi} [\phi(\phi) - \phi(-\infty)] - e \frac{\epsilon_2}{\pi} [\phi(\phi) - \phi(+\infty)] \quad (22)$$

where P_1 and P_2 are the bulk thermal pressures on each side of the

interface. Notice that this contact theorem differs from that of the permeable interface case [7]. Equation (22) is indeed satisfied by our microscopic expressions.

Additional sum rules and a more comprehensive discussion of this model will be given in future work.

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FIGURE CAPTIONS

Figure 1 Density profile. $m=0.5$ and $\sigma=-1$. Units are $e = \epsilon_1 = 1$.

Figure 2 Capacity as a function of the applied potential. $m=0.5$.

Figure 3 Electrocapillarity curve. $m=0.5$

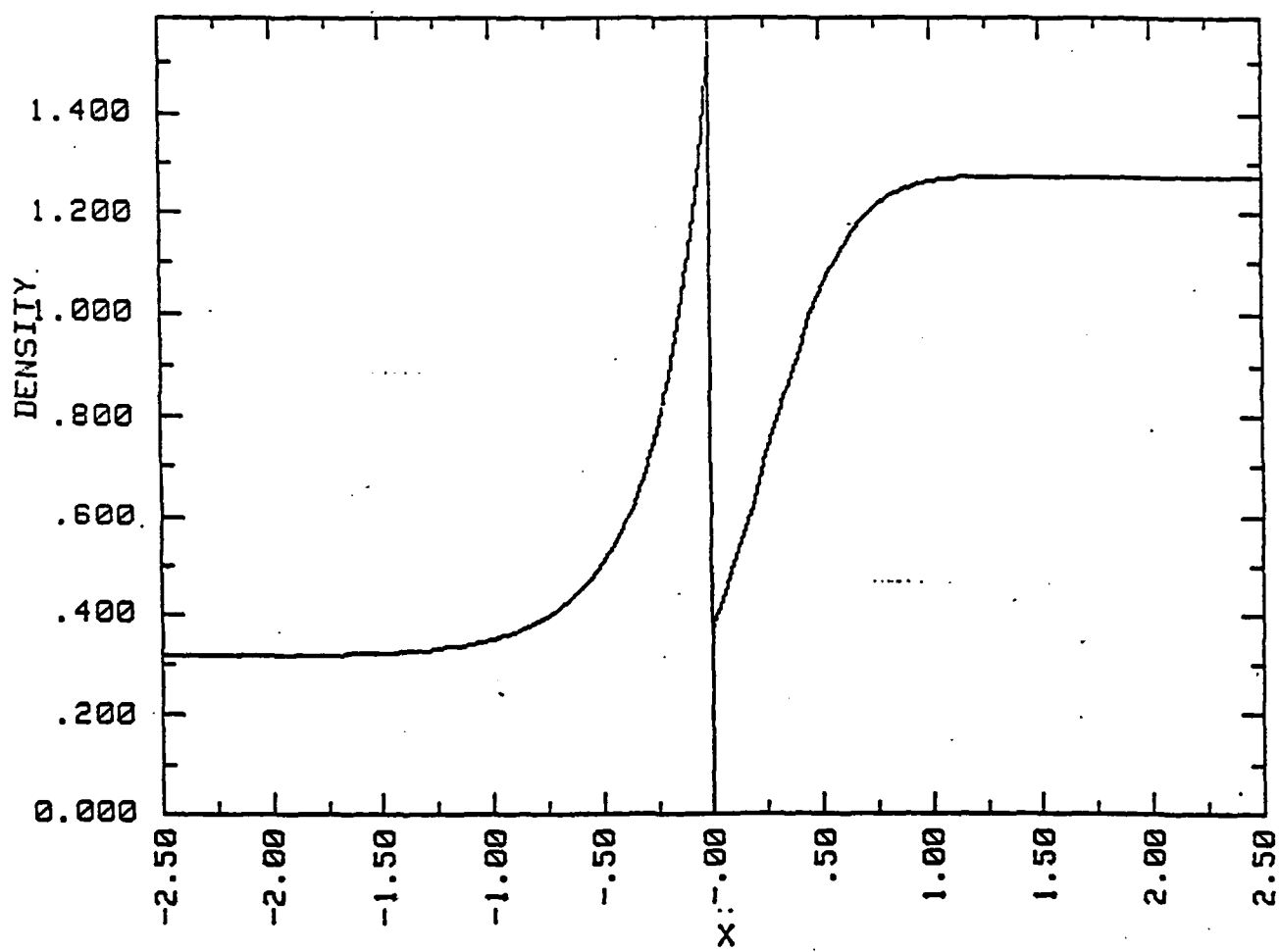


FIGURE 1

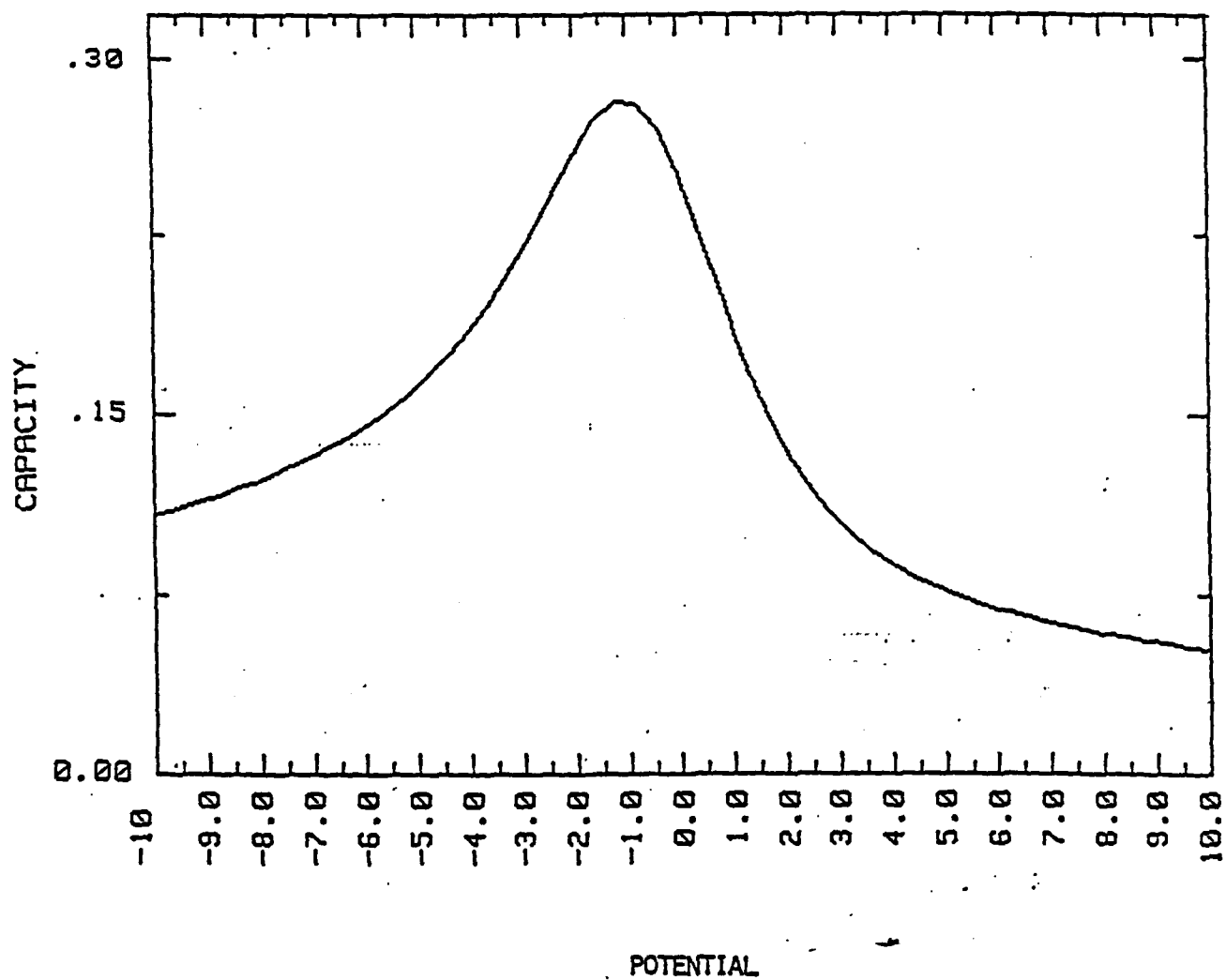


FIGURE 2

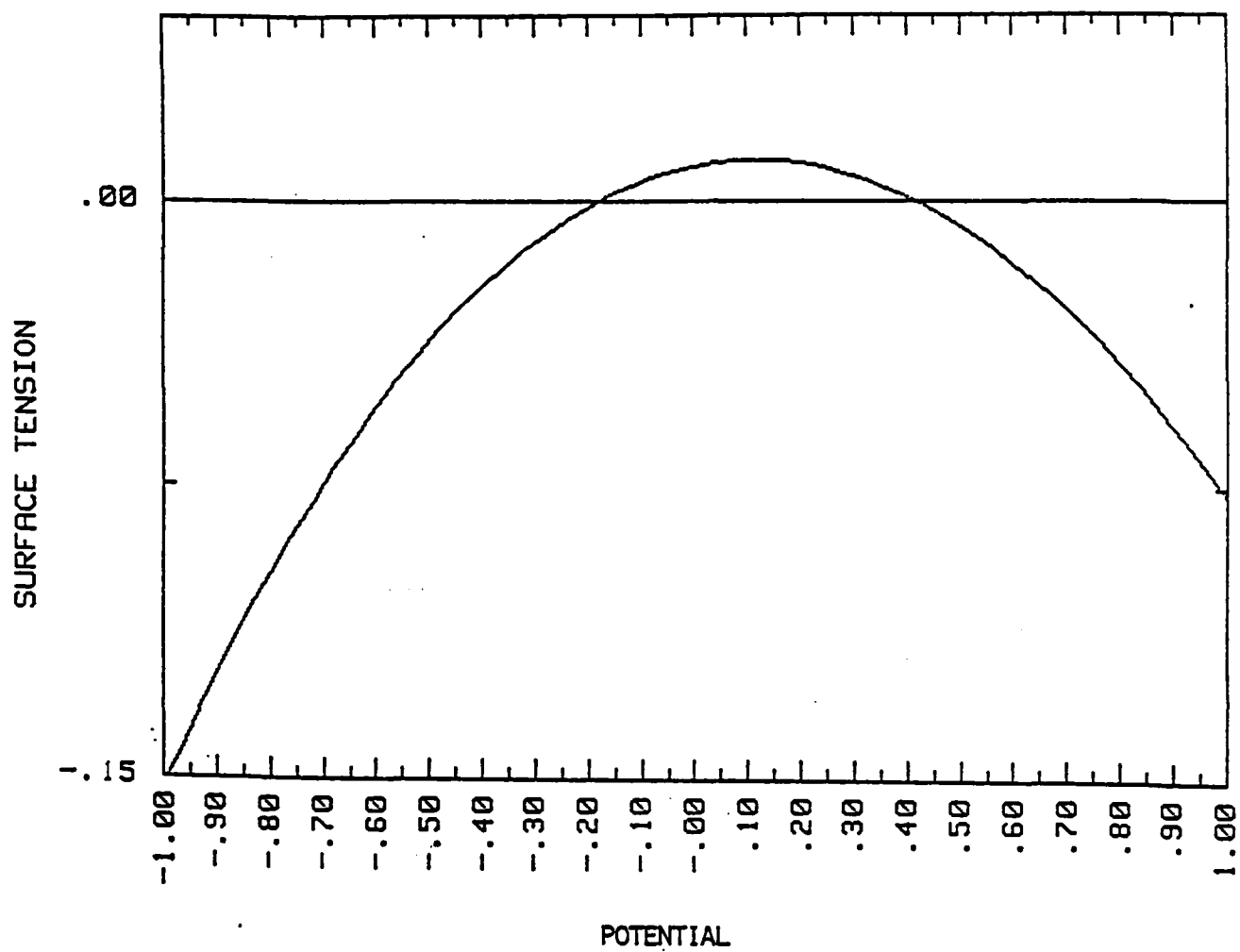


FIGURE 3

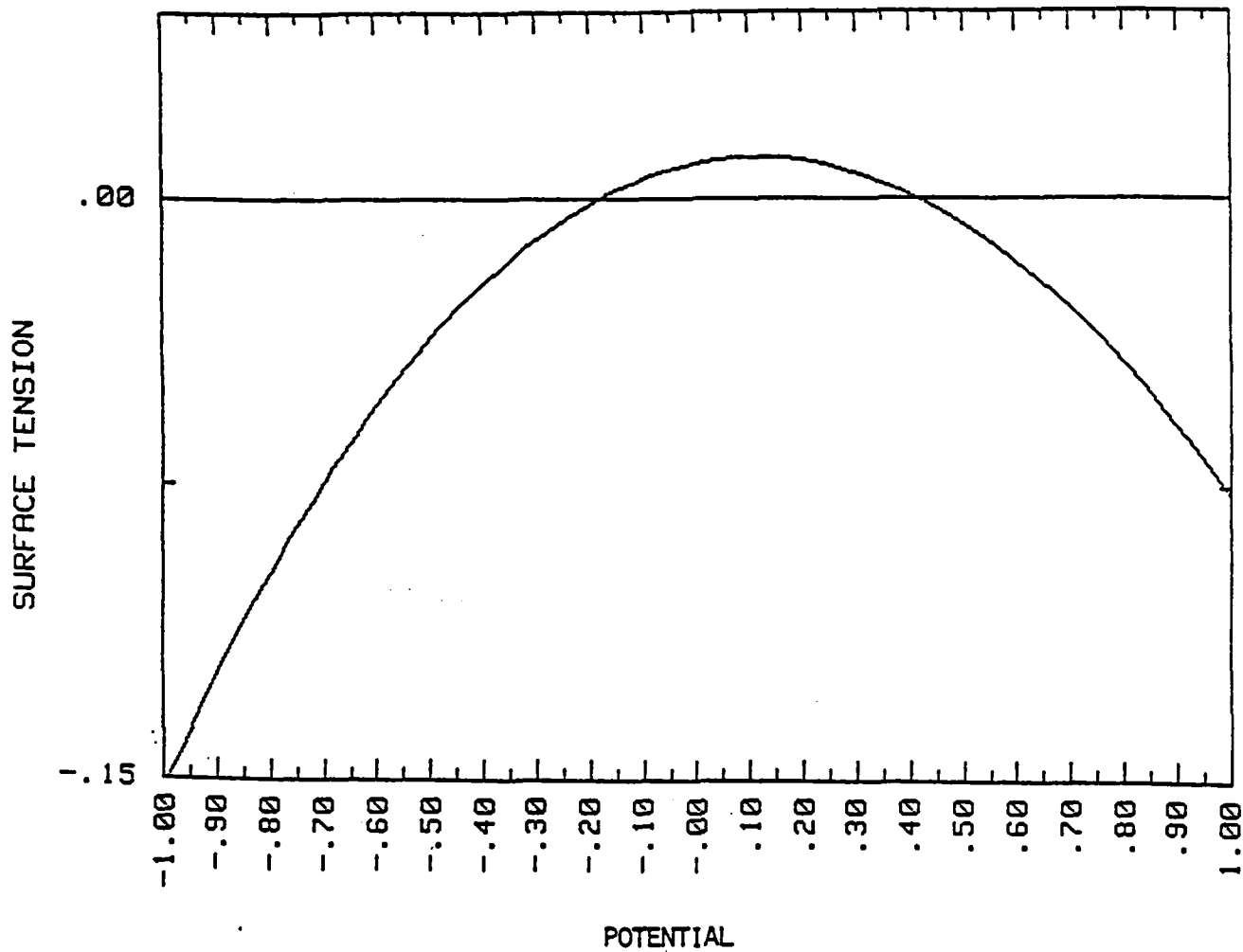


FIGURE 3

